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THE DETERMINATION OF SULFUR IN PETROLEUM OILS

BY

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B. S. Monmouth College, 1918

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY
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THE GRADUATE SCHOOL

MAY 31, 1922

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY GEORGE ROCKWELL BARNETT

ENTITLED THE DETERMINATION OF SULFUR IN PETROLEUM OILS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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Final Examination*

*Required for doctor's degree but not for master's

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THE DETERMINATION OF SULFUR IN PETROLEUM OILS.

I INTRODUCTION

The problem of determining the total sulfur content of petroleum oils confronted the writer in connection with an investigation of the efficiency of various metallic oxides in removing the sulfur. A large number of sulfur determinations were to be made, and for this reason a method was sought which would be simple of operation and rapid, as well as accurate, and at the same time applicable to petroleum oils widely varying percents of sulfur.

A search through the literature would convince one, at first, that it only remains for the chemist to pick at random any one of a large number of methods which have, seemingly, been tried out with success by various workers. Of course each is seen to have his preference, but it is apparently only a problem of making a list of the methods which the apparatus available to the particular laboratory will permit, and making the individual selection according to the temperament of the individual worker.

It has been the experience of the writer, however, that most methods prove to be disappointing. Although with practice one can obtain good checks with any procedure, the confidence temporarily placed in the process is dissipated when the results with one method are compared with results on the same oil

obtained by other methods.

Although all methods were not tried, the general experience has been the same. First comes the struggle to master the details of the method (in general involving more or less tedious procedure) to make each step in the process exactly the same in all cases in order to obtain good checks. Only to find in the end that the pursuit of check results has indeed been but the pursuit of a mirage, when it is seen that another method which gives equally good checks does not give the same results.

It follows, then, that check results mean little; that the same oil will analyze differently with different methods; and that the more methods used in determining the percent of sulfur in a certain oil, the greater is one's doubt as to how much sulfur it contains.

In view of these considerations, it was decided to lay the main problem of the removal of sulfur temporarily upon the shelf, until the matter of a satisfactory method for the determination of sulfur could be worked out.

II FORMS OF SULFUR PRESENT.

Unfortunately for the analyst the sulfur in petroleum does not occur in one form alone, but in a variety of forms. In spite of the well-known difficulty of isolating pure substances from such complex mixtures as petroleum and its fractions, a large number have been identified. When the latter are classified it is seen that the sulfur in petroleum is present not only in various types of organic molecules, but as free sulfur¹, and

sometimes as inorganic sulfates if the oil contains ground water emulsoids or inorganic solids in suspension².

For analytical considerations, it is well to keep in mind the forms in which the sulfur is present. For purposes of tabulation, the following are named: (a) free sulfur¹; (b) hydrogen sulfide²; (c) thiophenes⁴ and thiophanes⁵; (d) alkyl sulfides⁶; (e) mercaptans⁷; (f) carbon bisulfide⁸; (g) sulfonic acids⁹; (h) sulfonates¹⁰; and (i) alkyl sulfates¹¹. Inorganic sulfates mentioned in the previous paragraph are not usually considered in sulfur analysis, because water and solids are supposedly separated previous to the sampling.

III METHODS FOR SULFUR ANALYSIS.

It is seen that it is quite a problem to choose a combination of procedure and reagents that shall be efficient in converting all of the sulfur in its various forms to one certain form, and separate it from the other substances present without loss of sulfur at any point in the process. The fact that results by different methods disagree among themselves makes it self-evident that all of them are not efficient, as they should be, at least in the way they are applied. To the present there seems to be no one method which is applicable in all cases. Some of them seem altogether inapplicable. At the most, it seems that every method proposed is subject to special and often serious limitations.

The problem in sulfur analysis is, then, to find out which of the proposed methods give trustworthy results; and, if

possible, to find a new method or improve one of the old so that it shall be more generally applicable.

For future consideration it might be well, at this point, to review the possible methods which have been proposed for the determination of sulfur in petroleum oils or similar substances. They divide themselves into two main classes:

[1] Reduction to Hydrogen Sulfide.

The possibility of reducing all the sulfur to H_2S is interesting because the latter is easily and quickly estimated. The first attempt in this direction, as far as known, was that of Goetzl^{1,2}, in which he tried to gauge the amount of sulfur by the amount of H_2S which came off when the oil was distilled. Although it is known that oils containing no H_2S originally will evolve the gas when distilled³, no usable relation between the amount of sulfur present and the amount of H_2S evolved could be found. Next Waters⁴ attempted to hydrogenate an engine oil with gaseous H_2 in the presence of a catalyzer, oxidize the H_2S in an absorption solution of hypobromite, and precipitate the sulfur as $BaSO_4$. Catalyzers tried were metallic nickel and nickel oxide, and platinum foil. Waters recovered only a very small fraction of the total sulfur in this way.

The most promising attempt yet made seems to be that of Meulen⁵, by which he heats the substance in a combustion tube in a current of H_2 , passes the gases formed through a platinized asbestos catalyzer, and absorbs the H_2S in the effluents either in alkali and determines it iodometrically, or absorbs it in

sodium plumbite solution, and determines it colorimetrically. Meulen gives a table of comparative results on seven different petroleum fractions and two crudes, ranging from .024%-5.100% S, in which he compares the percents of sulfur obtained gravimetrically (method not stated) and obtained by his method. The results in each case check remarkably well in every case, being in some instances lower and in others higher than the gravimetric, but on the whole slightly higher. It would be interesting to know what gravimetric method he used for comparison.

Meulen's method is extremely interesting, because he applies it equally well on any petroleum or fraction of high or low sulfur content (and on other organic substances, such as coal). But in the opinion of the writer it is not, at present, to be viewed with undue optimism from the practical analytical standpoint. His samples (50 mg.) are too small to give good checks on any but the most sensitive balances, and with larger samples it would be expected that trouble would be had with rapid poisoning of the catalyzer, which was probably Waters trouble. In any event it is too early to state just what possibilities may lie in this method until it is further tried in other laboratories. No work has been done on this method in the present investigation.

[2] Oxidation to Sulfate.

To the second general class belong all of the so-called standard and rapid methods. All of them depend upon oxidizing the sulfur to sulfate, eliminating the residual oil (usually by complete oxidation), and determining the SO_4^{--} . For convenience,

the methods have been outlined as follows:

1- Digestion With Wet Oxidizing Agents.

(a) Strong KMnO_4 - Waters¹⁶.

(b) Nitric or fuming nitric acid- Waters¹⁷; Andrews¹⁸;
Francis and Crawford¹⁹; Calvert²⁰.

(c) Nitric or fuming nitric acid, and oxidizing agents-
Waters²¹; Gilpin and Schneeberger²²; Francis and
Crawford¹⁹; Gill and Grindley²³.

(d) Hydrogen peroxide- Lecocq and Vandervoort²⁴.

(e) Boil $\text{NaOH} + \text{Zn}^{++} + \text{Pb}^{++}$ to form PbS - Schulz²⁵.

2- Burning Methods.

(a) Lamp- Heusler²⁶; Engler²⁷; Friedlander²⁸; Magruder²⁹;
Ellerton³⁰; Conradson³¹; Lomax³²; Esling³³; Bordas³⁴;
Bowman³⁵; U. S. Bureau of Mines³⁶.

(b) In enclosed atmosphere of oxygen- Hempel³⁷; Grafe³⁸;
Marcusson and Doscher³⁹; Hauser⁴⁰.

(c) In combustion tube- Mabery⁴¹; Barlow and Tolleus⁴²;
Bay⁴³; Sauer⁴⁴; Dammer⁴⁴; Dennstedt⁴⁵; Brunck⁴⁶;
Vita⁴⁷; Lant and Lant-Ekl⁴⁸.

3- Open Fusion Methods.

(a) With alkalis- Eschka⁴⁹; Hundeshagen⁵⁰; Handy⁵¹; Heath⁵²;
Pertig⁵³; Sadtler⁵⁴; Garrett and Lomax⁵⁵; Parr⁵⁶.

(b) With mixtures of alkalis and oxidizing agents- Aufrecht⁵⁷;
Lidow⁵⁸; Peckham⁵⁹; Langmuir⁶⁰; Dubois⁶¹;
Schillbach⁶²; Blair⁶³; Charitschkoff⁶⁴; Koch and
Upson⁶⁵; Schreiber⁶⁶; Smith⁶⁷; Falciola⁶⁸.

4- Bomb Methods.

- (a) Oxidation with fuming nitric acid in a sealed tube under pressure- Carius^{69 70}; Anelli⁷¹; Roland⁷².
- (b) Oxygen Bomb- Filiti⁷³; Allen⁷⁴; Lord⁷⁵; Lohmann⁷⁶; Philip⁷⁷; Falciola⁷⁸; U. S. Bureau of Mines⁷⁹; Christie and Bisson⁸⁰; Parr⁸¹.
- (c) Sodium peroxide- Osborne⁸²; Konek⁸³; Parr, Wheeler, and Berolzheimer⁸⁴; St. Warunis⁸⁵; Lidow-Folde⁸⁶; Francis and Crawford⁸⁷; Franks⁸⁸; Parr⁸⁹.

5- Combination Methods.

- (a) Wet digestion followed by dry fusion with alkalis- Goetzl⁹⁰; Sanders⁹¹; Whittum⁹²; Rothe^{93 94 95 96}; Waters⁹⁷; Otsubo⁹⁸.

IV REVIEW OF METHODS.

In reviewing the oxidation methods under [2] , a strict historical presentation will not be attempted. The modifications will be taken up in the same order as the classification given in the outline.

In the wet digestion methods, Waters obtained low results when he attempted to oxidize the sulfur with strong KMnO_4 solution. He also obtained low results with the nitric acid digestion, even when adding such oxidizing agents as KClO_3 and KMnO_4 . Francis and Crawford came to the same conclusion regarding nitric acid digestion, with or without oxidizing agents, even though the digestion is carried out under a reflux condenser to prevent loss of sulfur. Andrews, however, claims good results when the reflux is used.

Gilpin and Schneeberger claim this method checks very well with the method of Carius, which will be mentioned later. Gill and Grindley vary this method by using KNO_3 as the auxiliary oxidizing agent. Lecocq and Vandervoort attempt to oxidize with H_2O_2 . Still another variation of the wet method is that of Schulz, in which he boils the sample in a strongly alkaline solution of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, to change the sulfur to PbS , filters, and fuses the residue with sodium and potassium carbonates. Inasmuch as the workers who have tried these methods are not agreed among themselves as to whether the results are to be trusted, it is thought doubtful if much confidence is to be placed in such style of attack.

Of the burning methods, by far the greatest amount of work has been done on the lamp method, and its modifications. This method adapts itself most readily to light burning fractions containing a very small percent of sulfur, on account of the fact that a much larger sample can be used than can be taken by other methods. The method simply consists in burning the oil itself (or mixed with a suitable solvent) in a lamp, catching the gases of combustion and passing them into an absorbing alkali. The apparatus needed can be improvised easily, but the method is objected to because it is long and tedious, and subject to error because of the retention of sulfur in the wick. However, if the lamp method is to be used, the latter objection can be overcome by running a sulfur analysis on the wick, according to Conradson. Or as suggested by Eordas, a bundle of capillaries can be used instead of a wick. On the whole, the lamp method is to be avoided

on account of the labor involved, except in cases of burning oils which have so little sulfur as to require a larger sample than can be taken in the oxygen bomb. For these fractions, the lamp method is considered the standard by the U. S. Bureau of Mines, and others, and is frequently used as a basis for reference.

Burning the sample in an enclosed atmosphere of oxygen is used by some workers. It consists of suspending the sample in a small container suspended in a large bottle (10-12 liters capacity) filled with oxygen. After the combustion an absorbing liquid is introduced. The method seems to have little to recommend it in the way of convenience of manipulation, and in addition incomplete combustions are troublesome. Burning the sample in a combustion tube in a stream of oxygen likewise has nothing in the way of simplicity of operation to recommend it. The method requires the usual combustion train, a platinumized asbestos catalyst to insure complete oxidation, and the reaction has to be kept down by a careful dilution of the entering oxygen by means of carbon dioxide. When properly controlled in every detail the method is accurate, but as a practical analytical procedure it is to be studiously avoided.

From the standpoint of simplicity of operation, fusing the sample in an open dish with alkalis, or a mixture of alkalis and oxidizing agents, would seem to be the choice procedure. The object is to catch the sulfur from the decomposing oil by means of the alkali present in intimate contact, completely oxidize the residual organic matter by open ignition, and precipitate the sulfur from a solution of the residue as BaSO_4 . The method

was first worked out by Eschka, and although more often applied to coal, has been used by some workers as a basis of reference for petroleum oils. The reagents most commonly used are MgO and Na_2CO_3 (2:1), known as Eschka mixture. This is mixed with the oil, sometimes leaving a layer of the Eschka mixture covering the surface during the burning. Or a double crucible arrangement can be used, whereby the escaping gases are forced to travel through 3-6 cm. of Eschka material before escaping. Very often, also, oxidizing agents, such as KClO_3 , KNO_3 , NH_4NO_3 , and $\text{K}_2\text{Cr}_2\text{O}_7$ have been used in conjunction with the Eschka mixture, or in special combinations without the latter. For example, Falciola mixes the substance before ignition with KClO_3 , KNO_3 , and NH_4NO_3 (4:1:1). Smith uses precipitated SiO_2 , Na_2O_2 , and KClO_3 . Schillbach uses BaO_2 , treats with HCl , filters all the soluble matter, and weighs the remainder as BaSO_4 .

A great deal of work has been done on these dry fusion methods, and the Eschka type of procedure has enjoyed a widespread popularity. A great many writers seem to regard it as a standard, although of late there is a tendency to question the accuracy of the results with the Eschka method. On the one hand a worker⁶⁸ is congratulating himself because his method checks so well with Eschka's, although giving slightly higher results; while on the other hand two in conjunction⁴⁸ condemn the Eschka method, claiming that on a high sulfur petroleum it gives 2.6% of total sulfur less than the actual sulfur content. On the whole the dry fusion method, with or without oxidizing agents, cannot be regarded with undue confidence at present. Part of the present investigation has been in

this direction, and will be covered further on.

Of the bomb methods, that of Carius was the first orthodox procedure, and was intended for use on any type of organic substance containing sulfur. The procedure is to seal the substance with nitric acid in a hard glass tube and heat until oxidized. The SO_4^{--} is then precipitated with Ba^{++} . Holand includes KClO_4 . Anelli claims more satisfactory results by introducing $\text{Ba}(\text{NO}_3)_2$ with the nitric acid. The Carius method doubtless gives reliable results on oils not too low in sulfur, but only small samples can be taken, and if the percent of sulfur is small the BaSO_4 obtained is so little as to be difficult of satisfactory manipulation. The method is also objected to on account of the danger of the tubes exploding.

Oxidation of the sample in a bomb under 30-40 atmospheres of oxygen is at present generally regarded as the most reliable method. About 1 gram of the oil is placed in a small metal crucible inside the bomb; a few cc's of water or alkaline absorbent placed in the bomb; the oxygen introduced through a one-way valve; and the sample ignited electrically. The sulfur is oxidized to SO_3 and unites with the water forming SO_4^{--} . Careful analysis of the residual gas has failed to detect the smallest trace of incompletely oxidized sulfur^{99 100}, when the proper oxygen pressure has been provided. For oils not too low in sulfur, this method is the standard in this country, as shown by the fact that it is so regarded by the U. S. Bureau of Mines and the U. S. Bureau of Standards, in references quoted. It is highly recommended by the best writers, and the main objection to it is that the apparatus

required is more costly than the ordinary laboratory can afford.

Cutting down the size of the bomb and eliminating the other special apparatus required with the oxygen bomb, the sodium peroxide bomb has come into favor. It is simple to operate, and with Na_2O_2 of standard purity the results are entirely satisfactory. However, the allowable sample is only half that of the oxygen bomb, so this method is even less adapted to low sulfur oils than the former. The procedure consists in placing the sample in the bomb together with about 14 grams of Na_2O_2 , and sometimes an accelerating mixture of benzoic acid and potassium chlorate. The ignition is started by heating the lower part of the bomb, after which the residue is dissolved in water, the solution acidified and boiled to decompose the H_2O_2 , the iron precipitated by ammonia and filtered, and the acidified filtrate treated with BaCl_2 to precipitate the SO_4^{--} . The article by Franks⁸⁸ is a good example of the careful application of this method in routine analysis on various oil fractions.

Another variation in the method of attack is a combination of wet digestion, followed by dry fusion with alkalis. Sanders, Whittum, Waters, and Otsubo treat the oil at first with nitric or fuming nitric acid, alone, or with an auxiliary oxidizing agent such as KBr or Br_2 . The mixture is heated and gradually brought to small volume, when an alkali is added and the organic matter is driven off by ignition. In the Rothe method the oil is placed in a flask with MgO , and then a large excess of fuming nitric acid is added. It is subjected to gentle heating for a time, and later ignited to decompose all the organic matter. In

all these cases the residue is treated with dilute HCl and filtered, and the SO_4^{--} in the filtrate precipitated with BaCl_2 .

Such methods are usually applied to low sulfur oils, because from 5 to 10 grams of sample can be taken, as compared with .5-1.0 gram in the bomb methods. More will be said later about this type of procedure, in connection with work done in the present investigation.

It is seen from the above that the selection of a method for determining sulfur is not always a simple one. The analyst must take into consideration, in the first place, the type of oil to be analyzed. Next, he must consider the accuracy necessary to the work at hand, the number of determinations to be made, the laboratory equipment available, and so on.

The type of oil to be analyzed has to be considered because there is no method which is perfectly adapted to all oils. The oxygen bomb method can be relied on to give dependable results with the widest range of oils of any other one method (Allen and Robertson¹⁰), but cannot be used on fractions of very low sulfur content because the sample is limited to one gram. The peroxide bomb method is very comparable, but the allowable sample is only half that of the oxygen bomb. The lamp method is adaptable to rather large samples, and when the proper precautions are taken gives dependable results, but even when inflammable solvents are used it can hardly be regarded as successful with heavy fractions. The Carius method is very seldom used because it is subject to the same limitations as are the bomb methods, and in addition has objectionable features of its own. Of the other methods or modifi-

cations cited, they are either held to be inaccurate, or accepted with reservations. Examples of the latter class are the Waters method and the Rothe method. Both are combinations of the initial wet oxidation with concentration of the sample, together with dry ignition at the end. Any type of oil can be used (although Vandaveer⁹⁶ applies the Rothe method to low sulfur oils only) and relatively large samples can be taken. If they give accurate results, the methods would seem to recommend themselves, from the standpoint of flexibility at least. Waters claims good results with his method, and gives comparative results with his method and others on the same oils. Good results are also claimed for the Rothe method⁹⁶. Investigation of the Rothe method formed part of the present work.

In considering accuracy, a method which is known to be inaccurate will find very little application. Since good qualitative methods are known¹⁹, in which a rough estimate of the amount of sulfur can be made, it is questionable whether an inaccurate quantitative method has any use at all.

The length of time required to make an individual determination is an important point to be considered, even when only an occasional analysis is run, and for routine work the tediousness of some methods is an absolute veto as far as they are concerned. Of the more dependable methods the bomb methods are about the speediest and the lamp method the slowest, with the Waters and Rothe methods in between.

As to the apparatus required, the oxygen bomb method involves the greatest outlay, including the tank of compressed oxygen

and fittings besides the bomb itself. The peroxide bomb is less expensive, but cannot be improvised. Apparatus for the other methods is of the ordinary laboratory type, or can be improvised.

V OBJECT OF THE PRESENT INVESTIGATION.

Such was the situation at the beginning of the present investigation. The object in view has been to try out various phases of sulfur analysis by several different methods; to see what methods seem to show the greatest possibilities for usefulness; and how they might be modified or improved. All in the hope that a method might be determined upon which would be reliable, simple to carry out, and applicable to a greater variety of oils than the methods now used. It cannot be claimed that such a hope was realized in the present work. But useful information was gained concerning the application of the methods tried.

VI EXPERIMENTAL.

The work done can be grouped roughly under four heads:

- (A) Application of the peroxide bomb; (B) Work on open fusion methods; (C) Work on the Rothe and Whittum methods; and
- (D) Determination of SO_4^{--} in solution.

(A)

The Parr peroxide bomb⁸⁹ is a simple and easily manipulated piece of apparatus, and its use in the complete oxidation of oil samples for sulfur determinations is becoming more and more popular. Some laboratories use this method almost exclusively. A

case in point is the work of Franks²², in which he analyzes shale oils and a complete series of shale oil fractions by this method.

The method, as applied by Franks, is as follows:

One measure of sodium peroxide (about 14 g.), 1 g. of powdered potassium chlorate and 0.2 g. of benzoic acid are placed in a Farr bomb and well mixed by shaking. About 0.5 g. of the uniform sample is weighed into this mixture by means of a medicine dropper and a small weighing bottle. The whole mass is then thoroughly mixed over a piece of glazed paper with a thin glass rod, any solids adhering to the rod or falling on the paper being subsequently returned to the bomb. After ignition in the usual manner the fusion is carefully dissolved in about 50 cc. of water, the bomb thoroughly washed with water, the inside being finally rinsed with about 1 cc. of concentrated HCl and a little more water, and the solution made acid with concentrated HCl. About 5 cc. of saturated bromine water is then added to oxidize all the sulphur to sulphuric acid and the iron to the ferric condition (if not already in that condition), and the solution boiled to decompose the H_2CO_3 and expel the Br_2 . Ammonia is added until the liquid is alkaline and the solution brought to a vigorous boil to coagulate the ferric hydroxide and expel the excess of ammonia [see 2, under MISCELLANEOUS POINTS]. The former is then filtered off, a small wad of absorbent cotton being placed in the bottom of the filter to hasten the operation and facilitate washing. Four thorough washings with hot water are sufficient. The solution is acidified with 1 cc. of concentrated HCl (using 40% orange indicator, adding 1 cc. in excess), made up to 225 cc., brought to a boil and 1 cc. of 10 per cent barium chloride solution is added slowly from a pipette. The boiling is continued until the precipitate is well formed, which sometimes requires as much as twenty minutes. About 200 cc. of liquid will remain. After standing over night the precipitate is filtered through a close 7 cm. filter paper (Munktell's No. 00 is preferred) and is carefully washed free from chlorides.

In general the method quoted is a good one, and could be questioned in few particulars. The writer tried varying proportions of KClO_3 and $\text{C}_6\text{H}_5\text{COOH}$, and found those given are about the best. Very few incomplete fusions were encountered when the accelerator was weighed out with fair accuracy, but failures were frequent if the right amounts were not used. It might be questioned if four washings of the voluminous $\text{Fe}(\text{OH})_3$ precipitate are enough to entirely free it from SCl_4 -. Efforts were made to demonstrate that slightly higher results would be obtained by dissolving the precipitate, diluting the solution and then precipitating the $\text{Fe}(\text{OH})_3$ again.

It was found in practice, however, that the added step in the procedure did little more than make it difficult to obtain good checks. In addition it increased the concentration of ammonium salts in solution, which is undesirable¹⁰². The amount of Barium chloride used can be criticised in this as well as most standard methods, but this point will be touched upon more fully under (D).

Using this method Franks obtains checks which are within one percent of error from their mean with oils containing .5% or more of sulfur, and successfully analyzes fractions containing as low as .3% of sulfur. The latter figure is perhaps about the minimum for satisfactory results with this method. This for the reason that with such small quantities of substance, a small loss of material or error in weighing would cause a relatively large error in the result. For example, with a .5 g. sample of oil containing .3% S, or .0015 g. S, corresponding to about 11 mg. of BaSO₄, an error of .2 mg. in one weighing would cause a 2% error if all the other operations in the analysis were perfect.

The peroxide bomb method was first tried on a sample of Louisiana crude oil, using the procedure given by Franks. Ten individual samples were analyzed to see how the checks were running. It was found that slight errors in weighing came out as large errors in the final results, but with careful work good results could be obtained and repeated. The last pair of samples came out .722% S and .732% S respectively. Thereafter the standard of agreement between checks was taken as .02% of total sulfur. It might be added, however, that such would be altogether unsatisfactory for oils of very low sulfur content.

The next oil tried by this method was a gasoline engine cylinder oil. The runs on this oil were of value only in demonstrating that this method could not be applied on such a low sulfur oil. Results obtained ranged between .03% S and .17% S.

A comparison between this method and the oxygen bomb method was made using a sample of California crude oil, which was the oil used in all later experiments on methods. Two samples analyzed 1.005% and .990%, giving a mean of .998% S, as compared with 1.003% S, the average of 4 determinations with the oxygen bomb.

In general the peroxide bomb method was found to check well with the oxygen bomb, without correction for sulfur in the reagents. Care was always exercised that the reagents were the best obtainable (the Na_2O_2 prepared especially for the purpose), and that they were not contaminated with laboratory vapors.

(E)

The simple technique of a dry fusion method is rather enticing to the analyst. If one could mix the sample with a small quantity of powdered reagent, burn it off, dissolve it and determine the sulfate from the solution, the question of routine sulfur analysis would be solved. A large number of samples could be weighed out and burned off simultaneously, nothing in the way of special apparatus would be required, and the operations would be easy.

An attempt was made to utilize the oxidizing principle of the peroxide bomb, by using Na_2O_2 mixed with various other substances to be ignited in an open dish. The advantage sought was that of using larger samples of oil than can be used in the peroxide bomb.

Mixtures of Na_2O_2 , MgO , and Na_2CO_3 (using 5 g. samples of California crude) were tried. The reagents were thoroughly mixed with the oil sample in a porcelain dish, then the mass was ignited by heating the dish cautiously. The object was to dilute the Na_2O_2 to such an extent that the fusion would travel quietly throughout the mass. It was found, however, that the oxidation was in all cases so vigorous, even when the oil and Na_2O_2 were greatly diluted, that particles of the reacting mass were always carried off in the flame. This held true even when the Na_2O_2 was entirely omitted from the mixture, except when only Na_2CO_3 was mixed with the oil. In the latter case the residue consisted of a caked material with carbonaceous matter imbedded in the mass. The latter could not be successfully burned to an ash, for it assumed a pasty consistency when heated.

Calcium peroxide^a was the next oxidizing agent tried. It was first mixed with Na_2CO_3 , but the activity seemed to be slight. Then the CaO_2 was mixed with the oil alone and heated. Oxidizing action was evident, the mixture giving off dense fumes during the action. The most encouraging feature with the CaO_2 was that the mixture after ignition was light and powdery, containing very little carbon, and that easily burned off. The method was tried quantitatively by mixing 10 g. CaO_2 with about 3 g. of oil. This

^a Sample from Bausch and Lomb Optical Co., known to have been in stock over 15 years. Not more than a trace of sulfur in it. Another sample, commercial grade, was tried but it was loaded with sulfate. For the last trials a new sample of CaO_2 was obtained, which was fresh and much more reactive than the previous samples. It contained a small amount of sulfate, but blanks were run in every case.

mixture was ignited by carefully heating one edge of the dish, when the fusion would start spontaneously and creep throughout the mass, white fumes being given off meanwhile. After the reaction was completed the organic matter was completely burned off, the ash dissolved in HCl and filtered, and the SO_4^{--} in the filtrate precipitated with BaCl_2 . Average of the two samples was .383% S on the California crude containing 1.0% S. When a large amount of the CaO_2 was taken (20 g. with 1.5 g. oil), the result was .579% S, after correcting for blanks on the reagents, which correction was made in every case in this phase of the work.

The next oxidizing agent tried was BaO_2 . It was hoped that the method proposed by Schillbach⁶² could be used. It is the most direct method that has ever been proposed. It consists in mixing the sample with BaO_2 , heating the mixture to start the reaction, burn off any residual carbon, dissolve the ash in HCl and weigh the insoluble matter as BaSO_4 . Various proportions of BaO_2 and oil were tried, but the reaction always ended in a melt which was hard to free from residual carbon and formed a hard, horny mass when cooled. It was found that this horny residue would become more friable upon standing in moist air, but the method was abandoned because of the difficulty of igniting the residue to a satisfactory ash.

A desirable ash could be obtained, it was found, by using a mixture of BaO_2 and CaO_2 , and some runs were made with this mixture. After correcting for a large tare in the blanks, the resultant sulfur was only .412%. This was in using CaO_2 of doubtful strength, however, so a new sample was obtained. The reaction

with the new CaO_2 in the mixture was much more vigorous than with the old, but the net result was about the same. In fact it was found that all the runs made with the BaO_2 or mixtures thereof had such a high sulfur content in the blanks as to make the results erratic. When so much sulfur was present in the reagents, and the latter were weighed out on rough balances, little could be hoped for in the way of accuracy. Qualitative tests on the reagents individually showed not more than a trace of sulfur in the new sample of CaO_2 , but the BaO_2 which had been used all along, and which was supposedly pure, was found to be loaded with sulfate.

Attempts to use the fresh CaO_2 alone were unsuccessful because the reaction was so vigorous that considerable of the reacting mixture was thrown out of the dish. It was tried in a beaker covered with a watch glass and also a lightly covered flask, with the same condition obtaining. A mixture of CaO_2 and BaO_2 had been tried in a small steel bomb and the bomb exploded, so the CaO_2 alone was not tried in a bomb. Sodium carbonate was tried as a diluent with the CaO_2 , but the percent sulfur given by this method was .650%, or roughly two-thirds of the actual sulfur content. The proportions used were, 10 g. CaO_2 , 8 g. Na_2CO_3 , and 1.5 g. of oil. Using half the amount of reagents in the same proportion, with about the same amount of oil, resulted even lower, .541% S.

In concluding the trials with the open fusion method, it may be said that the results are disappointing. Although an accurate open fusion method may be developed, possibly, none of the methods tried to date are accurate. If it is a choice between the Eschka method, and the CaO_2 - Na_2CO_3 method last tried, the writer would

choose the latter. It is easy to manipulate, but even with the oxidizing agent present the results are low.

Open dry fusion methods proposed are all subject to loss of sulfur. There is no doubt that a considerable amount of the sulfur content of the oil is lost through volatilization of light fractions in the initial stages of the reaction, and although the presence of oxidizing agents may help to conserve the sulfur at this point, the loss is still appreciable. Where the reaction is at all vigorous there is also the tendency of mechanical loss. On the other hand, if the reaction is not vigorous enough, and much carbonaceous matter is left in the end, the sulfur already caught in the alkali may be lost again through reduction to decomposable sulfites by the incandescent carbon or CO present in the burning off. Loss in this ^{way} was later proven in connection with experiments on the Rothe and Whittun methods.

(C)

Whittun⁹² developed a combination method at the University of Illinois, and some further data concerning it was obtained by Otsubo⁹⁸. The method was first proposed as a substitute for the lamp method and intended for light burning oils. An effort was made to prove its reliability, and also to extend its use to a wider variety of fractions. The procedure is as follows:

Weigh 5-10 g. of the oil into a porcelain dish. Dust .2-.5 g. of finely powdered K₂Cr₂O₇ over the surface. Add 4-5 cc. of fuming nitric acid, drop by drop, with constant stirring. After the reaction has ceased, place the dish on a steam bath or asbestos pad and evaporate the liquid until it becomes viscous. Add about 2 g. of Ischka mixture and mix thoroughly with the oil, being careful to take up all the oil that may adhere to the sides of the dish. Place the dish over an alcohol flame, or

Bunsen protected with an asbestos pad, and allow the mixture to dry slowly. The heat should be increased gradually until the mixture catches fire and burns to a white powder, breaking up the large particles occasionally with a glass rod. After cooling add water and HCl to dissolve the residue and filter the solution. The SO_4^{--} in the filtrate is precipitated in the usual manner.

Leaving aside the question of whether the method retains all the sulfur in lamp oil, its behavior with crude oil was studied. Certain difficulties were encountered using this method with crude oil, and considerable work was done to try to eliminate them; and, when the procedure could be modified to suit a heavier oil, to see what results could be obtained by it.

The first difficulty encountered was in the addition of the fuming nitric acid. Even adding it very slowly, drop by drop, the reaction was always so violent that some of the oil would spatter out. Benzene was tried as a diluent to cut down the violence of the reaction somewhat. The spattering was diminished by the benzene, but not entirely eliminated. The results of duplicate samples using the benzene were a trifle higher than those obtained by the straight Whittum method, so it was seen that the diluent in no way effected loss of sulfur. It was then resolved to try inert solvents. Chloroform, tetrachlor ethane, and carbon tetrachloride were tried, and of these the latter seemed the best. Quantitative runs using different amounts of CCl_4 failed to show any diminution in the amount of sulfur obtained, and the results were in some cases higher. It was concluded that the addition of enough CCl_4 to cut down the violence of the reaction had no undesirable effect, and was to be recommended. The method is to mix the CCl_4 , say about 15-20 cc., with the oil and then to add the fuming nitric

acid slowly.

The next difficulty met in the Whittum method was that, if the sample were heated for a time to concentrate the residue after the addition of the fuming nitric acid and before adding the Eschka mixture, the mass would solidify when it was attempted to stir in the latter, and a uniform mixture was impossible to obtain. It was found that a good mixture could be obtained if the Eschka reagent were mixed with the oil directly, or very shortly after the reaction with the fuming nitric acid had subsided.

Another mechanical difficulty that was encountered was the fact that when igniting the Eschka mixture at the end to completely burn out the residual carbon, the mass would assume a pasty consistency and be hard to handle. This could be obviated by increasing the proportion of MgO in the mixture.

As the chief mechanical difficulties seemed to have been met, quantitative runs were made on the California crude oil, of 1.0% sulfur content. The Whittum method modified only by adding the Eschka mixture directly after the reaction with fuming nitric acid had ceased gave .684% S. The same, except that an inert solvent was added before the fuming nitric acid, gave .727% S. Varying the amounts of fuming nitric acid and of MgO and Na_2CO_3 , results were obtained: .758%, .768%, .734%, .813%, and .749%. It was found that a larger percent of sulfur could be obtained by increasing the amount of fuming nitric acid to about 7 cc. A larger percent of Na_2CO_3 in the absorbing mixture had the same effect, but the limit for the method was the highest figure given, .813% S, and this was obtained without correcting for sulfur in the reagents. Also

the larger amount of Na_2CO_3 used made the residue difficult to handle, and it was ignited for several hours in the effort to obtain a white ash. It is probable that in this time some sulfur was absorbed from the laboratory fumes.

It was thought that perhaps an absorbent present at the time the fuming nitric acid were added would conserve the sulfur. Anhydrous MgCl_2 was first tried, for the reason that it would in no wise take up the energy of the oxidizing acid as would MgO or Na_2CO_3 , and could at the same time unite with the less volatile SO_4^{--} , HCl escaping. But only .328% of sulfur was obtained in this attempt.

Another modification was tried, by using anhydrous SeOCl_2 as the oxidizing agent. Some very interesting reactions ensued, chief among which was the escape of reddish fumes of selenium. Some of the sulfur was oxidized to SO_4^{--} , and the residual Se was easily gotten rid of in the end by volatilization during the subsequent ignition of the residue. But the oxidation was either incomplete or selective, for the percents of sulfur obtained by the SeOCl_2 were .278% and .290% in two runs.

The last trial of the Whittum method was made about as the first, using the larger amount of fuming nitric acid with smaller samples (2.5-3.0 g.), and then during the ignition with the Eschka mixture, the dishes were piled full of MgO to force the escaping gases to travel through a thick layer of absorbent before they could escape. The fact that 1.108% of sulfur was obtained in this run was not taken as proving that all the sulfur could be obtained by this method, but rather as an indication that other sources of

error were being multiplied, e.g., high concentration of Mg salts causing occlusion in the BaSO_4 precipitate; and sulfur in the reagents, for which no correction was made. In later experiments it was proven that in this general type of procedure the sulfur is lost in two ways: by volatilization during the addition of the fuming nitric acid, and by reduction to SO_2 and consequent volatilization or otherwise in the burning off of the residue. In view of these facts it will be seen that even if all the sulfur could be retained in the burning of the residue, by passing the escaping gases through a large quantity of absorbing alkali, there would still have been the loss encountered at the initial stage in the analysis. The Whittum (and Rothe) type of sulfur analysis was held to be inherently at fault in these respects, at least as applied to crude oils. Reasoning by analogy it might be questioned whether such methods are reliable on low sulfur oils. Of course the total error in sulfur with a low sulfur oil would be small, in proportion with the small amount of total sulfur, but the results by the Whittum type of procedure might still be questioned.

The method of Waters is essentially the same as the Whittum method, except that Waters uses fuming nitric acid which is saturated with bromine. This method was not tried in the present investigation.

The Rothe method has come into some favor, as shown by the fact that it has been tentatively adopted by the A.S.T.M.; and the recent work of Vandaveer⁹⁶ would seem to recommend it. The principles of the method are the same as in the Whittum method, variations in procedure being that the operation is carried out

in a flask, that the absorbing material (MgO) is added before the addition of fuming nitric acid, and that a large excess of the latter is used. The procedure recommended by Vandaveer:

Weigh from 5 to 10 grams of oil into a liter pyrex flask containing 2 grams of magnesium oxide. Immediately add carefully 25 cc. of fuming nitric acid. Allow the mixture to stand until the reaction ceases. Then heat gently on a sand bath for about three quarters of an hour. At the end of that time gradually raise the temperature until all the nitrates are decomposed. Continue the heating over a full Bunsen flame for several minutes. Blow in air or oxygen and heat the flask with a free flame to drive off the carbon. Cool the flask, moisten the white residue with water, add concentrated hydrochloric acid and heat. Filter off the carbon and precipitate the sulfur as barium sulfate in the usual manner.

Six analyses were made of the California crude oil by the Rothe method. The first two (without modification, except that 500 cc. flasks were found to be more convenient, on the whole, than liter flasks) gave .685% S. The next three, modified by adding 20 cc. of CCl_4 before treatment with the fuming nitric acid, gave .782%, .786%, and .751%, respectively. The last was low again, .686% S. Taking the average of the three in closest agreement, the result by the Rothe method is .773% of sulfur, as compared with .734% of sulfur, the average of the ten best by the Whittum method, or modifications.

It can be concluded from the above that the Rothe method gives slightly better results than the Whittum method, but loss of sulfur occurs in both cases. Also, the fact is further demonstrated that addition of an inert diluent for cutting down the violence of the reaction with fuming nitric acid, does not incur additional loss of sulfur. And in case of the Rothe method it was found that, using the crude oil, such an inert diluent is necessary to prevent the mixture taking fire when the fuming nitric

acid is added. The CCl_4 used served as an excellent preventative in this respect.

The Rothe method was also tried on a sample of heavy Mexican crude oil, which analyzed 4.940% of sulfur by the peroxide bomb method. The Rothe method gave 1.670% of sulfur. Apparently the higher the sulfur content of the oil, the greater is the loss in sulfur by the Rothe or similar methods. It might well be argued that the converse is true: that the lower the percent of sulfur in the oil, the more accurate is the method; and that inasmuch as the Rothe method has been used largely for low sulfur oils, it is in no wise to be condemned because it gives unsatisfactory results with high sulfur oils. Such may be the case, but the writer is of the opinion that the same principles which govern the loss of sulfur with a high sulfur oil would also pertain to a low sulfur oil. If so, the Rothe method could only be applied on oils so low in sulfur that the loss of sulfur by the method comes within the experimental error. It would be necessary to make a whole series of comparative runs on a series of oils of gradually differing sulfur content to find out exactly where this point is. Even then there would be the uncertainty as to whether the method would be equally accurate with two oils of the same total sulfur content, but of different properties. The difficulty with the method is to know where to draw the dividing line- which analyses to trust, and which to view with suspicion.

It might also be argued that the type of sulfur compounds in low sulfur oils are easily handled by the Rothe method, but that the method is not designed to oxidize the free sulfur or some of

the more refractory sulfur compounds of crude oils. The argument is hardly tenable, however, since fuming nitric will readily and completely oxidize free sulfur to sulfuric acid. It seems that loss is incurred by such factors as premature volatilization and loss in the burning off rather than by insufficient oxidizing strength to attack all the forms of sulfur.

To obtain some idea as to just where the loss of sulfur is incurred in these methods, approximately 30 g. of the California crude oil were taken in a large porcelain dish, with 50 cc. of CCl_4 , and about 2 g. of KBr. Thirty cc. of fuming nitric acid were added with stirring, and after the reaction had subsided the dish was warmed gently for a time to concentrate the mixture. Before it became too viscous, about 10 g. of Fehle's reagent was added and the whole thoroughly mixed with a steel spatula. The residue was then moulded into a circular cake and quartered, two opposite quarters being taken for ignition in the regular Whittum style, and three representative samples being taken from the remaining quarters for ignition in a peroxide bomb. The latter analyzed .700%, .716%, and .709% sulfur respectively, or an average of .708% S. The samples burned off in the usual Whittum style analyzed .576% and .597% S, or an average of .587% sulfur.

It is seen from this experiment that $\frac{100(.708-.587)}{.708} = 17.1\%$ of the sulfur is lost in the burning off of the oily alkali residue in the Whittum method. The total loss of sulfur by the Whittum method (taking the average of ten runs, of .734%) is seen to be $\frac{100(1.0-.734)}{1.0} = 26.6\%$ of the sulfur originally in the oil. Of this total loss, the remaining 9.5% (26.6%-17.1%) of the original sul-

fur evidently is lost by volatilization in the initial stage of the process.

In concluding the discussion of this phase of the work it seems evident that approximately one fourth of the total sulfur of the crude oil in question is lost in the methods which depend upon initial oxidation with fuming nitric acid, together with ignition of the residue with alkalis. Of the sulfur lost, roughly one third is lost by volatilization in the initial stage when the fuming nitric acid is added, and the remainder is lost by reduction to SO_2 and consequent escape, or otherwise in the ignition of the residue. It is not claimed that these proportions would hold for other types of oils, but at least it seems certain that sulfur is lost at both points, and that such a loss would be incurred in a greater or less degree with any oil.

(D)

The problem of sulfur analysis has not been entirely solved by any means when the sulfur is obtained as SO_4^{--} in solution ¹⁰³ ¹⁰⁴ ¹⁰⁵, notwithstanding the fact that most methods usually conclude the details of the procedure by some such statement as, "And the sulfur in the filtrate precipitated with BaCl_2 in the usual manner."

As intimated, the standard procedure is to precipitate the SO_4^{--} from the slightly acidified solution by means of BaCl_2 , weigh the precipitate as BaSO_4 and calculate to percent of sulfur in the sample.

For the best work, after boiling the mixture it should be

allowed to stand over night to allow the BaSO_4 precipitate to form into as large crystals as possible, and this is a slow procedure. Even without standing over night, the usual gravimetric procedure is somewhat slow and tedious.

For more rapid work there are several modifications which can be used with very little sacrifice in accuracy. Chief among these are the Parr photometric method¹⁰⁶, and the method whereby the sulfur is precipitated as benzidine sulfate with subsequent titration of the latter by KMnO_4 in acid solution^{107 108}. Another method, of the volumetric type¹⁰⁹, is to add an excess of BaCrO_4 to the solution. The reaction will go slowly to completion towards the formation of BaSO_4 . The amount of BaSO_4 formed can be determined indirectly by titrating the equivalent amount of CrO_4^{--} left in solution by means of standard iodine. Still another method, this of a semi-volumetric nature, is that proposed by Bucherer¹¹⁰. Here the solution is diluted to 500 cc., and standard BaCl_2 solution is added to aliquot portions, the exact amount to be added being determined by filtering off a few cubic centimeters each time and testing the small filtered portions with a drop of H_2SO_4 or a drop of BaCl_2 to see which is in excess.

None of these methods were tried in the present investigation. Their usefulness lies chiefly where routine sulfur determinations are to be made daily, where with a careful standardization of procedure very good accuracy can be obtained.

The Parr photometric method is doubtless the most rapid of those given. It requires a special form of photometer, but in laboratories making routine sulfur analyses the latter would be

a justifiable outlay. The method is to make up the solution to be tested to 250 ccs., taking 50 cc. of this solution, diluting to 100 cc. and adding an excess of sized BaCl_2 crystals. This results in a finely divided, non-settling precipitate. The turbidity of the solution is a direct factor of the amount of sulfur, which can be obtained by direct translation of the photometer reading by means of a curve. The method is surprisingly accurate, when the eye of the operator has once been standardized by comparison with solutions of known sulfur content. It has another advantage, also, that the relative error is no greater with a low percent of sulfur than with a high percent.

The method using a BaCrO_4 suspension as the precipitant is interesting; but it is thought doubtful if the method proposed by Bucherer would be found satisfactory.

The recognised standard procedure, however, is the gravimetric estimation of the BaSO_4 precipitate. It is also the most practical when only occasional analyses are to be run. As there are points which are too often lost sight of, some of the variable factors of this precipitation were tried out from a practical standpoint.

Since it is a well-known fact¹⁰³ that BaCl_2 is apt to be adsorbed or occluded in a precipitate of BaSO_4 when it is forming, one would expect to find that standard methods for sulfur analysis would lay down a careful procedure to prevent such occlusion. There seems to be a laxity in this respect. Holde, the U. S. Bureau of Mines, the U. S. Bureau of Standards, and Hamor and Padgett¹¹² (in references cited) simply say that the precipitation of BaSO_4 is

made with BaCl_2 in the usual manner, except that in the Mines Bulletin No. 5, the directions are to add BaCl_2 solution drop by drop until there is an excess present. Parr precipitates by means of the addition of 10 cc. of 10% $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, regardless of whether the oxygen bomb, Eschka, or peroxide bomb methods are used. Franks adds 5 cc. of 10% BaCl_2 , using the peroxide bomb method. On the whole, it seems to be customary in oil analysis to add 10 cc. of 10% barium chloride solution.

Since too much BaCl_2 in solution may introduce an error in the results, the question arises as to just how much to add, and in what manner, so that the error caused by occlusion of BaCl_2 in the BaSO_4 will be reduced to a minimum; and at the same time have enough Ba^{++} present to completely precipitate the SO_4^{--} . From the standpoint of common ion effect, it would seem desirable to have a certain excess of Ba^{++} in solution, to decrease the solubility of the BaSO_4 to be recovered.

Consulting a table of solubility data¹¹¹, the solubility of BaSO_4 in water at room temperature is 2.5×10^{-3} g. per liter. Say precipitation was made in 400 cc. of solution, from the fusion of .5 g. of oil (the amount taken by the peroxide bomb method), this would mean that the sulfur which would go undetected, with no excess of Ba^{++} , could be only .027%, due to the solubility of BaSO_4 in water.

Treadwell-Hall¹⁰³ recommends the addition of 10 cc. of N. BaCl_2 for each gram of BaSO_4 precipitate to be obtained. With this standard, let us assume an analysis of a .5 g. sample of oil containing 1% of sulfur, and see what percent of sulfur could remain

undetected in solution. The solubility product of BaSO_4 is 1.21×10^{-10} , or .000000000121. In the sample is .005 g. of sulfur, which is equivalent to .03635 g. of BaSO_4 . According to our standard, we shall therefore add .3635 cc. of N. BaCl_2 .

Amount of BaCl_2 added, in grams03795

Theoretical amount necessary03365

Amt. BaCl_2 in excess of theoretical00435

This amount of BaCl_2 in excess of the amount necessary to precipitate all the sulfur from 400 cc. of solution is equivalent to .0000376 gram ion concentration of Ba^{++} , BaCl_2 being 72% ionized. The Ba^{++} concentration due to the BaSO_4 in solution is .000011, giving a total Ba^{++} concentration of .0000486 g. ion.

$$(\text{Ba})(\text{SO}_4) = .000011 \times .000011 = .00000000121$$

$$(\text{SO}_4) = \frac{.00000000121}{(\text{Ba})} = \frac{.00000000121}{.0000486} = .00000249.$$

BaSO_4 in solution is the same or .00000249 moles per liter. This is equivalent to .00023 g. of BaSO_4 in 400 cc. of solution, and on the .5 g. sample is equivalent to .0063% of sulfur.

In the same manner, the amount of sulfur which could go undetected, owing to the solubility of BaSO_4 in water, using the amount of BaCl_2 solution called for by Treadwell-Hall, in a .5 g. sample containing 2% of sulfur, would be only .0036%. Applying the same solubility data to an actual analysis of a sample of Mexican crude oil: sample, .5232 g., analyzing 4.814 % S, the amount of sulfur which went undetected in this way was only .0015%.

Of course the solubility of BaSO_4 is somewhat affected by presence of various salts in solution, as well as free acid, but such effects are usually slight except for the presence of acid

(and the trivalent metals such as iron, which are removed by ammonia). The acidity can be regulated by adding 1 cc. of HCl to the neutral solution before addition of the BaCl_2 .

It will be seen that in all these cases the amount of sulfur which could go undetected owing to the water solubility of BaSO_4 in the presence of only a small excess of Ba^{++} is well within the experimental error, and therefore to be disregarded.

Then why add a larger excess? There is the practical reason, of course, and that is the uncertainty of the amount of BaSO_4 precipitate to be obtained. Even from this standpoint it would hardly seem desirable to add so much BaCl_2 as 10 cc. of 10% in all cases, regardless of the method or the size of the sample. When using the peroxide bomb method Franks has cut the usual amount of BaCl_2 in half, and yet he is adding enough for the complete precipitation of 13.2% of sulfur, considering the necessary excess and the size of the sample taken. With the usual amount in the peroxide bomb method, enough BaCl_2 is added to precipitate 26.4% of sulfur.

From a practical standpoint, does this unnecessary excess of BaCl_2 usually obtaining actually effect the results appreciably? The following results answer the question:

Analyses By The Parr Peroxide Bomb.

| | % S obtained by adding 5 cc. of 10% BaCl_2 soln. | % S obtained by adding amt. BaCl_2 called for by Tread- well-Hall | Increase in app- erant % of S due to addition of too much BaCl_2 |
|------------------|--|--|--|
| Louisiana Crude | 0.835 % | 0.727 % | 0.108 % |
| Mex. Crude No. 1 | 4.940 | 4.814 | 0.126 |
| Mex. Crude No. 2 | 4.983 | 4.819 | 0.164 |

In every case the filtrate was tested with a drop of H_2SO_4 to

Make sure that BaCl_2 was in excess.

In view of these considerations, it would seem advisable to take into account the size of the sample and the probable maximum percent of sulfur present when adding BaCl_2 , and not add an unnecessary excess. In the opinion of the writer, the method given in one reference of adding the BaCl_2 solution drop by drop is not a practical one, for with small amounts of sulfur no precipitate of BaSO_4 is visible at first, and only after boiling does it appear. When it is seen as a turbidity, and it is a practical impossibility to gauge the amount of the precipitant which should be added. The latter condition also holds true for larger amounts of sulfur.

The manner of adding the BaCl_2 also has something to do with whether it is occluded in the BaSO_4 precipitate. The best practice is to dilute the necessary amount of BaCl_2 to 100 cc. and add it hot to the boiling hot solution to be precipitated. The addition is made slowly, with stirring. In ordinary routine work, however, it should be satisfactory in most cases to add the BaCl_2 in a 10% or a 5% solution, being careful to add it slowly and with constant stirring to the boiling hot solution.

VII MISCELLANEOUS POINTS IN OIL SULFUR ANALYSIS.

1-General.

The most convenient method for weighing oil samples was found to be a weighing bottle which has a medicine dropper ground into a tight joint at the neck. This was easy to handle, and prevented volatilization of the oil.

Reagents should be the best obtainable, and laboratory fumes should be carefully excluded. Blanks should always be run on each new lot of reagents, and more often if necessary, as impurities crop up where least expected. A case in point during the present investigation was a fresh bottle of Merck's "pure" BaCl_2 , which was found to contain a high percent of SO_4^{--} .

It is advisable to run blanks on every fresh packet of filters, by selecting about four from different parts of the pack. It was found in practice that the weight of the incinerated filter which had been treated exactly as the sample was always higher than that given on the label.

For routine work it is sometimes convenient to use Gooch crucibles, but they have to be carefully filled with digested and washed asbestos fiber. It is easy to go wrong with Gooch crucibles in ignition work.

In igniting the precipitates a blast should not be used, for BaSO_4 decomposes slowly at the temperature of the blast lamp. There is also danger of blowing particles of BaSO_4 out of the crucible.

2-Peroxide Bomb.

Attempts to guess out the amounts of accelerator reagents to be used result in frequent incomplete fusions. These should be weighed with fair regard for accuracy. For speed of manipulation it was found convenient to weigh out the accelerator in doses, folding the doses in small papers. These papers of doses can be bunched into packets, and are then in convenient form to add immediately without loss of time during the runs.

In precipitating out the iron, a good excess of NH_4OH should always be added, or else some of the sulfate may be held in combination in the precipitate as basic ferric sulfate. For the same reason, the solution should only be heated enough to coagulate the $\text{Fe}(\text{OH})_3$ sufficiently for good filtration. See Treadwell-Hall¹⁰².

The $\text{Fe}(\text{OH})_3$ precipitate should be well washed with hot water, for gelatinous precipitates are notorious for retaining soluble salts. When it is considered that it takes from 10 to 20 washings to entirely rid the BaSO_4 precipitate from chlorides, it does not seem reasonable to suppose that 4 washings of the $\text{Fe}(\text{OH})_3$ precipitate are sufficient, as stated by Franks.

TABLE I

Comparative Results By Different Methods- Otsubo⁹⁸

Results by the methods given:

| Oil | Oxygen Bomb | Peroxide Bomb | Whittun-Otsubo |
|------------|-------------|---------------|----------------|
| Mex. crude | 3.79 % S | 3.97 % S | 3.76 % S |
| Light oil | 0.587 | 0.580 | 0.528 |

TABLE II

Comparative Results By Different Methods-Vandaveer⁹⁶

Results by the methods given:

| Oil | Peroxide Bomb | Whittun | Lothe-Vandaveer |
|-----------------------|---------------|---------|-----------------|
| Fuel oil | 0.367 | 0.331 | |
| Fuel oil ^a | 0.340 | 0.360 | 0.408 |
| Kerosene ^a | 0.037 | | 0.040 |
| Color oil | 0.295 | | 0.211 |
| Crude | 0.430 | | 0.200 |
| Crude | 0.200 | | 0.187 |

^a The only instances given in which results by the wet and dry combination methods were not lower than in the bomb methods.

NOTE: Results given on this page are averaged results from the references cited.

TABLE III

Test Runs on California Crude Oil

| Method | Percent S. | Average of --samples. |
|---|------------|-----------------------|
| Peroxide bomb method; samples about .5 g.; Duplicates shown checked within .015% sulfur | 0.998 % S | 2 |
| Oxygen bomb method; samples about .9 g.; individuals, .988%, 1.028%, .993% S | 1.003 | 3 |

AMOUNT OF SULFUR IN CALIFORNIA CRUDE taken to be 1.000 per cent.

TABLE IV

Experimental runs on California crude.

| Method. | Percent S | Samples |
|---|-----------|---------|
| Whittum, anhydrous HgCl_2 in dish with oil | 0.328% | 2 |
| Whittum, but SeCCl_2 the oxidizing agent | 0.278 | 2 |
| Whittum, but SeCCl_2 the oxidizing agent | 0.290 | 2 |
| Whittum, Eschka directly after fuming nitric | 0.684 | 2 |
| Whittum, oil diluted with benzene | 0.727 | 2 |
| Whittum + 10 cc. CCl_4 | 0.758 | 2 |
| Whittum + 15 cc. CCl_4 | 0.768 | 2 |

TABLE IV (continued)

| Method | Percent S | Samples |
|--|-----------|---------|
| Whittum, CCl_4 and 7 cc. fuming nitric acid | 0.734 | 2 |
| Whittum, CCl_4 + 7 cc. fuming nitric + 2 g. MgO + 4 g. Na_2CO_3 | 0.813 | 2 |
| Same as previous, except 12 cc. fum. nitric | 0.749 | 2 |
| Whittum, large amt. Eschka heaped over dish | 1.108 | 1 |
| Average by the selenium oxychloride | 0.284 | 4 |
| Average most representative Whittums | 0.734 | 10 |

TABLE V

California crude by the Pothe method.

| Method | Percent S | Samples |
|--|-----------|---------|
| Without modification ^a | 0.685 | 1 |
| T.enty cc. CCl_4 added before the fuming nitric | 0.782 | 1 |
| Same as previous | 0.751 | 1 |
| Same as previous | 0.786 | 1 |
| Same as previous | 0.686 | 1 |
| Representative average | 0.773 | 3 |

^a Five hundred cc. flasks were used in all experiments with the Pothe method.

TABLE VI

Open fusion experiments with the California crude.

| Method | Percent S | Samples |
|---|-----------|---------|
| 10 g. CaO_2 + 3 g. oil | 0.383 | 2 |
| 20 g. CaO_2 + 1.5 g. oil | 0.579 | 2 |
| 10 g. CaO_2 + 6 g. BaO_2 + 2 g. oil | 0.412 | 2 |
| 10 g. CaO_2 (fresh) + 3 g. Na_2CO_3 + 1.5 g. oil | 0.650 | 2 |
| 5 g. CaO_2 (fresh) + 4 g. Na_2CO_3 + 1.5 g. oil | 0.541 | 2 |

TABLE VII

Comparative runs on Mexican crude.

| Method | Percent S | Samples |
|---------------|-----------|---------|
| Peroxide bomb | 4.940 | 2 |
| Rothe | 1.670 | 2 |

VJII SUMMARY AND CONCLUSIONS.

1. A review has been made of the various methods which have been proposed for the analysis of sulfur in petroleum oils or similar substances.
2. Methods where the oil is fused in open dishes with alkalis or mixtures of alkalis and oxidizing agents are held to be inaccurate, due to loss of sulfur. Efforts to modify the general procedure, together with the trial of new oxidizing agents to prevent such loss of sulfur, have not met with success.
3. The Whittum and Rothe methods, whereby the oil is treated with liquid oxidizing agents, followed by dry fusion of the residue, were also tried out with crude oils. Loss of sulfur was found in every case, and efforts to modify the methods were unsuccessful in preventing such loss.
4. It was demonstrated that loss of sulfur, as shown under 2 and 3, is occasioned at two points: (a) loss by volatilization of the oil in the preliminary stage; and (b) loss by reduction or otherwise in the burning off of the residue.
5. Addition of an inert solvent to the oil before treatment (by wet oxidizing agents) does not diminish the efficiency of the oxidation, and has the advantage of preventing loss of sample occasioned by too violent a reaction.
6. Good results have been claimed for the Whittum, Waters, and Rothe methods when used on low sulfur fractions, but in view of the inaccuracies found in the Whittum and Rothe methods as applied to crude oils, there is also reason to doubt the accuracy

of such procedures with low sulfur oils.

7. As far as the present work would show, the only practical methods of sulfur analysis which can be viewed with entire confidence are the oxygen bomb and the sodium peroxide bomb methods, which can be applied to medium or high sulfur oils; and the lamp method, which is resorted to with very low sulfur oils. The Carius method and the combustion tube method, although accurate, are not held to be generally applicable. The Meulen reduction method is subject to the same objection.

8. It is shown that too much barium chloride solution is frequently added to obtain the best results.

9. Miscellaneous points are given in connection with oil sulfur analysis.

10. Tables of data are given showing analyses of oils by different methods.

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